I. FILM AND DIELECTRIC CHARACTERISTICS OF HYDROCARBONS WITH POLAR ADDITIVES

II. INSTRUMENTAL EVALUATION OF PHOTOCHEMICAL STABILITY OF SOME IMPORTANT PHARMACEUTICAL CONSTITUENTS

BY

DAVID WILCOX CARLEY

B.S., Knox College, 1944
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AN ABSTRACT OF A THESIS

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I. FILM AND DIELECTRIC CHARACTERISTICS OF HYDROCARBONS WITH POLAR ADDITIVES

Introduction

This investigation was carried out for the purposes of correlating various properties of lubricating oils containing polar additives, and of instituting new methods for measuring the properties. The properties include polarity, film-thickness on a vertical metal surface, film-strength, and optical properties.

Other important properties, not specifically treated in this work include oiliness, specific gravity, viscosity and surface tension.

The past decade has witnessed great strides in the development of beneficial additives for lubricating oils, made necessary by more drastic refining methods which remove many of the naturally occurring inhibitors and antioxidants, and by demands for heavy duty performance.

Previous film-thickness and strength measurements were made by Clark and Gallo (1), and Clark, Parks and Culmer (2), Shell Oil Company (3) and Langmuir, Blodgett and Shaefer (4). Previous experiments on certain optical properties of the oils have also been demonstrated (5).

Additives whose function is to increase oiliness (6) contain one of the groups $C=O$, $(PO_4)^{3-}$ $(OH)^-$ etc., and are adsorbed on metal surfaces. These are known as polar additives. They may serve as wear prevention agents by a simultaneous corrosion of high spots and a polishing action. Several examples of this type of action are demonstrated in this work by use of a revised Almen machine. A very definite protective coating is formed upon the surface of the bearing.

Experimental And Discussion

Two methods for measuring film thickness were used. The

first was basically the same as that described by Clark, Parks, and Culmer (2). The second utilized the Gardner Thickness Gage. This instrument consists of a small disc of stainless steel about one-half inch thick and two inches in diameter. The edge is double grooved around the entire circumference, with the center ridge slightly out-of-round. A scale reads the thickness at the point where the out-of-round ridge begins to wet its surface. Results between the two methods agreed closely — so closely in fact, that the difference could be attributed to experimental error.

Since agreement was so close, it is reasonable to recommend that the Gardner Gage be used as a standard instrument for measuring oil film thicknesses.

A rather surprising result of this phase of the work shows that one particular non-additive oil is a better film former than most additive oils. This could possibly be due to the destruction of a natural "film-forming" additive which was removed by refining operations. Time-thickness curves are shown for all oils.

Film strengths were obtained using a Hayes revision of the Almen machine. This is a set-up whereby a constantly increasing pressure is exerted on the outside of a bearing which is immersed in the oil. Generally speaking, non-additive oils produced a much weaker film than did the additive oils.

Dielectrics were measured on a capacitance bridge. No significant differences could be detected between the oils with additives and those without. And no correlation seemed to exist between polarity and film strength or thickness.

Spectrophotometric measurements were recorded with a Coleman Spectrophotometer, before and after a severe heat treatment in the presence of finely divided iron and aluminum. The curves showed clearly that some profound chemical and structural changes indicative of deterioration from oxidation and sludge formation occurred in lubricating oils under

severe conditions of use; but it was not possible to correlate in any simple manner the changes in transmission with the properties which may have altered. Nor was it possible to resolve the highly characteristic low wave length dip in the Coleman Spectrophotometer curves on the Beckman or G-E spectrophotometers.

II. INSTRUMENTAL EVALUATION OF PHOTOCHEMICAL STABILITY OF SOME IMPORTANT PHARMACEUTICAL CONSTITUENTS

Introduction

Many pharmaceutical products undergo a decomposition when exposed to ultraviolet rays. The extent of deterioration varies among the essential oils and is a serious problem with manufacturers of perfumes, cosmetics, tooth pastes, etc. This work attempts to measure the deterioration, semi-quantitatively, and to develop a ruby glass which will minimize or prevent the photodecomposition (7).

A series of essential oils, diluted with 95% ethanol, was radiated with ultraviolet light and the extent of photodecomposition of the major constituent determined from the change in their absorption in the ultra-violet range. The Carey Recording Spectrophotometer was used to obtain all absorption data.

Dobrovolny (8) developed a copper-ruby glass using Cu_2O and stated that a metal cyanide was necessary as a reducing agent. This was a direct contradiction to Charan (9), who said that a ruby glass could not be made using a cyanide reducing agent. Actually, neither was entirely

correct.

Experimental And Discussion

The following essential oils and compounds thereof were used in the investigation: bergamot (natural and imitation), jasmine, cloves, lavender, cassia, petitgrain, verbena, heather, spearmint, peppermint, Vitalis hair dressing, Mum bouquet, cinnamic aldehyde, Ipana mixed oils, Trushay lotion, Mum deodorant lotion, Bufferin and methyl salicylate.

Absorption curves were obtained for all oils, plotting the wave-length against optical density. Each oil showed peak densities at characteristic wave-lengths and the height of the peaks was taken as an indication of the amount of major absorbing constituent present. The lowering of the optical densities was plotted against time of exposure to ultraviolet.

All oils showed at least some deterioration, though heather, cloves, petitgrain and methyl salicylate showed remarkable stability against ultraviolet radiation. The most sensitive were cassia, bergamot and cinnamic aldehyde.

An attempt was made to determine any beneficial effects of red glass (7) which absorbs radiation below 560 mμ upon heather, bergamot or cinnamic aldehyde — either by destroying an oxidation accelerator or producing a inhibitor. Samples were irradiated first in a red container, then in a clear one. Identical samples were irradiated only in the clear bottle. No evidence of a beneficial wave length could be detected in those exposed first through the red glass. However considerable protection against photochemical deterioration is provided by bottling the oils in ruby glass containers, in comparision with clear glass.

A further test for a beneficial band was performed on methyl salicylate and spearmint oil. Samples of each were irradiated under a series of Farrand filters — each varying in its transmitted light by approximately 25 mμ and covering the range 400-700 mμ. The 618 and 640 mμ filters had a very

specific and marked effect upon spearmint oil. The effects on methyl salicylate were noticeable but not as pronounced.

In the production of copper-ruby glass, several compositions showed promise of being suitable. A typical composition which gave a good ruby color was the following:

SiO_2	55.0	gms.
K_2CO_3	5.0	
Na_2CO_3	20.0	
$CaCO_3$	6.5	
Al_2O_3	1.75	
Cu_2O	0.20	
SnO	0.10	
Bi_2O_3	0.02	
Fe_2O_3	0.15	
CaH_2	1.0	

The SiO_2 content was reduced slightly from the usual amount to obtain better melting in small batches.

Foremost among the results was the fact that CaH_2 proved to be an excellent reducing agent and substitute for NaCN. It was also shown that Sn and/or Bi are not necessary constituents of copper-ruby glass. However the depth of the color was not as intense without Bi or Sn. The depth of the red color also appeared to increase with the amount of Cu_2O and Fe_2O_3 present, within certain limits. The Fe_2O_3 was useful in reducing the transmission of the glass in the near infra-red. Beyond a certain limit Fe_2O_3 produced opaqueness. Also it was shown that the rate of cooling can substantially affect the depth of color and the homogeneity of the glass. If cooling takes place too rapidly streakiness is likely to appear, particularly when working with small batches. This ruby glass provides effective protection against photochemical change of any system sensitive to rays in the ultraviolet or visible parts of the spectrum below 560 $m\mu$ or in the near infrared (1μ).

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VITA

The author was born on June 21, 1922 in Galesburg, Illinois. He attended the public schools of that community and was graduated from Galesburg High School in 1940. He entered Northwestern University in September of 1940, transferred to Knox College, Galesburg, Illinois in September of 1941, and was graduated, with honors, from that school in December 1943 with the degree of Bachelor of Arts. He was employed by George Washington University from January 1944 to June 1944 as a research assistant. In July 1944 the writer entered the Navy as an Ensign and spent the following two years as communications and executive officer on an LST.

In June 1946 the author entered the Graduate College of the University of Illinois. From January 1947, until he received his degree of Master of Science in Chemistry, he was a research assistant on the University of Illinois Rare Earth Research Program sponsored by the Office of Naval Research. In July 1947 he accepted a position as Chemical Process Engineer with C. F. Braun & Company in Alhambra, California, working on oil refinery process design.

In September 1949 the author re-entered the University of Illinois. For the next two years he held a half-time teaching assistantship in the division of Analytical Chemistry.

The author is a member of the American Chemical Society and Sigma Xi.